Development of Sensitive and Selective Biosensors for Electrochemical Determination of Biological Molecules: A Cyclic Voltammetric Study

Final Synopsis of the Thesis submitted

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By

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Introduction

Electrochemical sensors and biosensors have great scientific impact because, they have many applications in assessment of complicated matrices such as clinical, food, environmental and pharmaceutical sample. Nowadays usage of electroanalytical methods for the different applications has been increased as compared other analytical methods. Electroanalytical measurements are popular due to the advantages like inexpensive, rapid detection and high sensitivity, and selectivity with excellent detection limit [1-5]. Other analytical methods like HPLC, GC-MS, LC-MS and chemiluminascence are expensive and time consuming, consumes more solvents-, reagents, and needs experts for handling [6]. Among different types of voltammetric experiments cyclic voltammetry (CV) and differential pulse voltammetry (DPV) are major focus of our research work. CV is an electroanalytical technique in which the current at a working electrode is determined as a function of applied voltage. It is a dynamic and repeatedly used voltammetric tool to analyze the oxidation and reduction of the electroactive molecules. CV technique has versatile applications such as qualitative and quantitative analysis of organic and inorganic compounds, adsorption process, electron transfer, reaction kinetics, thermodynamic properties of solvated molecules, fuel cell, supercapacitor, and battery studies. Also, CV coupled HPLC is effectively used for the investigation of complex mixtures. DPV is also a voltammetric tool in which voltage is changed using pulses of increasing amplitude and the current is sampled before and after each voltage pulse. Pulse voltammetric techniques are more sensitive than CV, because the non-faradaic current is more in CV while in pulse methods it is negligible. Generally DPV is used to determine analyte at trace levels [7-10].

Carbon materials (graphite flakes, multiwalled carbon nanotubes, graphene, pencil graphite etc.) were extensively used in material science for different types of applications such as electrochemical sensors, drug delivery system, supercapacitors, microchips, fuel cells, energy

storage devices, etc. High usefulness of carbon materials is due to their mechanical, electrical, thermal, and microelectronic and stability characteristics. There are plenty of electrochemical sensors based on carbon materials are reported for the determination of electrochemically active species. The carbon based materials most suited materials for the fabrication of sensors because they possess exceptional characteristics like extensive potential domain, strong absorption capacity, porosity, low ohmic impedance, biocompatibility etc. [11-15].

Chemical modification of electrode is a strategy to improve the analytical characteristics of electrode. Electrodes are modified with different molecules such as nanomaterials, monomers, surfactants, ionic liquids, acid treatment, etc. The modification of electrode significantly lower the over potentials, yields high current signals and high stability without the fouling effect [14-19]. In our work we have fabricated sensitive sensors based on surfactant immobilization, electropolymerizastion, acid treatments and bulk modifications.

Summary of the Thesis

The effort of the research is to formulate the voltammetric sensor devices by modifying the carbon electrodes such as pencil graphite electrode, carbon paste electrode, and carbon nanotube paste electrode, graphene paste electrode through electrochemical polymerization, acid treatment, surfactant immobilization and bulk modifications. The modified and optimized sensors are used for the electrochemical investigation of biologically important molecules. The electrochemically active organic molecules such as riboflavin (RF), curcumin (CUR), dopamine (DA), pyridoxine (PY), phloroglucinol (PL), vanillin (VA) and cetirizine (CTZ), indigotine (IT), paracetamol (PC), rutin (RU) and levofloxacin (LFN) were analysed using new approaches. The important molecular properties were studied such as reaction mechanism, number of electron transfer, rate constant, electrode process, electrode sensitivity and selectivity towards the sensing of molecules. Finally proposed strategy is employed for real time analysis.

Thesis outline

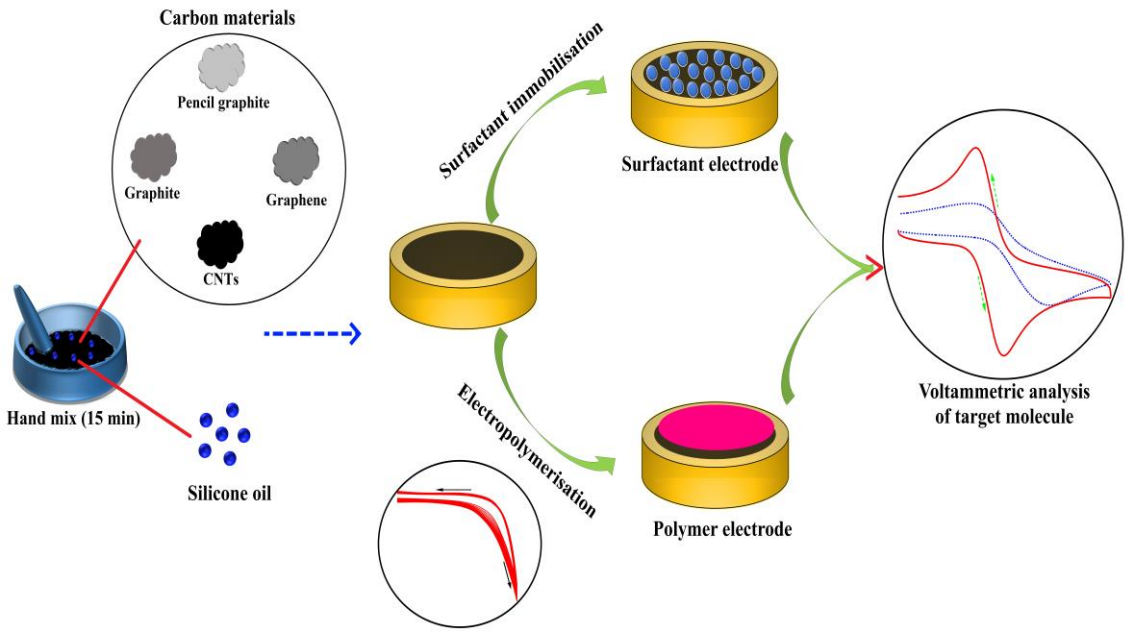
The thesis entitled “Development of Sensitive and Selective Biosensors for Electrochemical Determination of Biological Molecules: A Cyclic Voltammetric Study” is divided into 12 chapters.

Chapter 1: Introduction

This chapter covers the introduction, electroanalytical methods, theory and analytical applications. A review of electrochemical approaches for determination of biological molecules and objectives of the research are explained in this chapter.

Chapter 2: Experimental

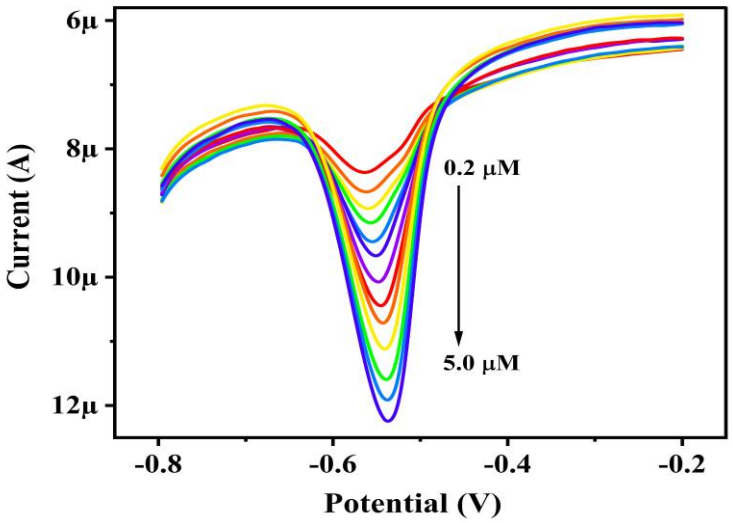
This chapter includes basic electrochemical apparatus (potentiostat, a recording device, and an electrochemical cell), electrodes arrangement (counter/auxiliary, reference and working electrodes) and experimental protocol. Chapter also describes preparation of bare and chemically modified carbon electrode in detail.



Chapter 3: A Surfactant Enhanced Novel Pencil graphite and Carbon Nanotube Composite Paste Material as an Effective Electrochemical Sensor for Determination of Riboflavin

(**Journal of Science: Advanced Materials and Devices,** 5, 2020, 56-64. **IF: 5.46**)

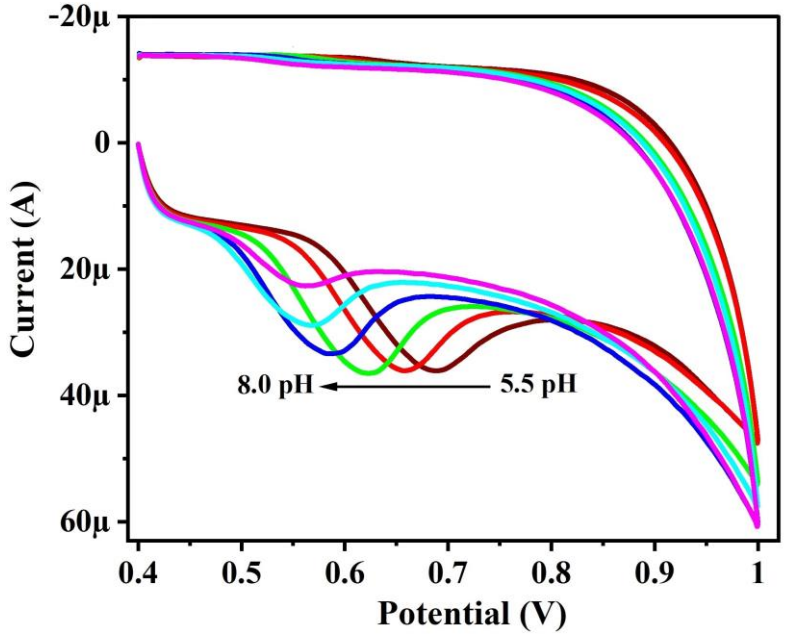
This chapter describes a novel sensor fabrication using anionic surfactant sodium lauryl sulphate modified carbon nanotube and pencil graphite composite paste electrode (SLSMCNTPGCPE) is prepared and characterized using Field Emission Scanning Electron Microscope (FE-SEM) and CV. The SLSMCNTPGCPE is a responsive electrode material for the determination of RF as compared to carbon nanotube and pencil graphite composite paste electrode (CNTPGCPE) and bare pencil graphite paste electrode (BPGPE). The fabricated sensor shows a linear current response to a diverse concentration of RF in 0.2-0.8 µM and 1.0-5.0 µM with a low detection limit of 1.16 $\times 10^{-8}$ M by applying DPV. The stability, reproducibility, repeatability, interference and concurrent investigation with DA have been done with satisfactory outcomes. The new sensor was applied for the RF estimation shows good recovery in B-complex pill and natural food supplement.



Chapter 4: Surfactant and Polymer Composite Modified Electrode for the Sensitive Determination of Vanillin in Food Samples

(ChemistrySelect, 6, 2021, 2700-2708. **IF: 2.109**)

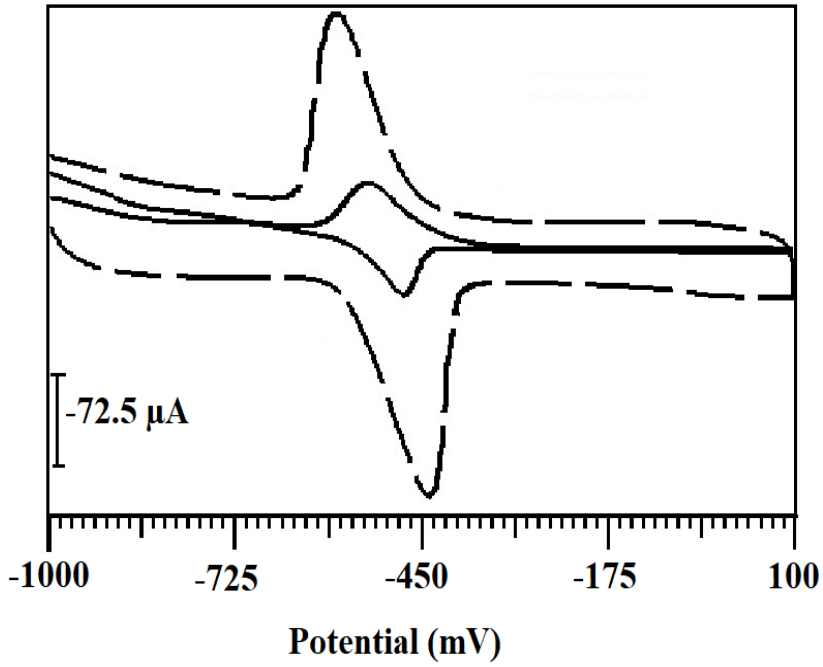
In this work, the active poly (titan yellow) and octoxynol-9 modified carbon nanotube paste electrode (PTOMCNPE) was prepared and characterized through a FE-SEM, Energy-dispersive X-ray Spectroscopy (EDX), and EIS. It promotes the detection and quantification of VA. The electrochemical parameters such as the number of electro polymerization cycles, effect of surfactant amounts, influence of pH, and scan rate were optimized to get an enhanced current signal for the targeted molecule. Under calibrated conditions, the concentration linearity for vanillin was 2.0-40.0 µM using both CV) and DPV. The LOD for determination VA was found to be 4.9×10^{-8} M and 9.31×10^{-8} M using DPV and CV respectively. The stable and selective sensor was applied to food samples with excellent recovery.



Chapter 5: Determination of Riboflavin at Carbon Nanotube Paste Electrodes Modified with an Anionic Surfactant

(**ChemistrySelect**, 4, 2019, 2168 –2173. **IF: 2.109)**

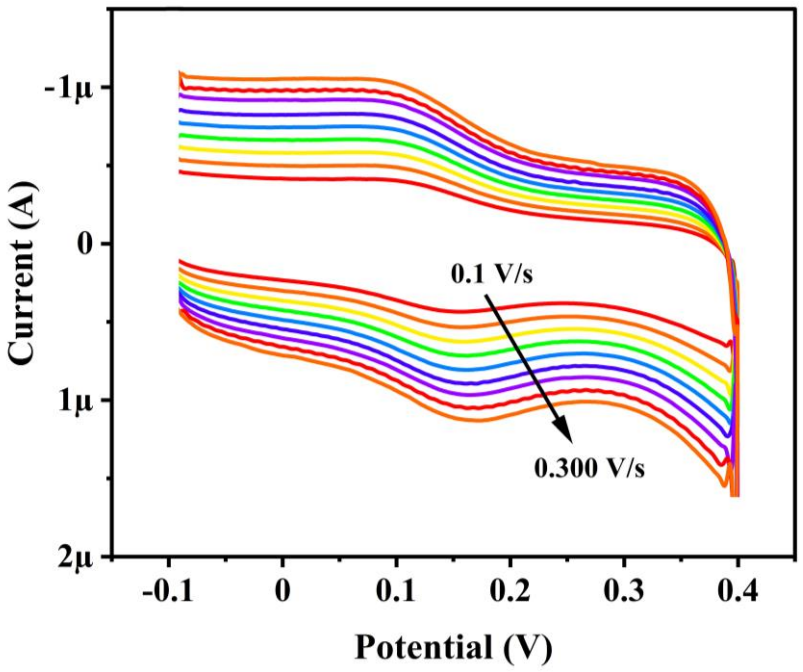
A Sodium lauryl sulfate modified carbon nanotube paste electrode (SLSMCNTPE) was fabricated for the electroanalysis of RF in phosphate buffer solution (PBS) at pH 7.0 by CV. The electrode was found to be a very sensitive tool for detection of RF; it was shown that SLSMCNTPE yields a high current response towards RF as compared to the bare carbon nanotube paste electrode (BCNTPE). Key parameters were optimized for RF determination. The effects of surfactant concentration, pH, scan rate and concentration of RF on the oxidation peak current values were determined. The RF oxidation peak appeared at -440 mV and reduction peak at -575 mV vs. saturated calomel electrode (SCE). The SLSMCNTPE revealed good repeatability, reproducibility, stability, high electrochemical sensitivity in its voltammetric response and a detection limit of 9.25×10^{-8} M.



Chapter 6: Poly (glutamine) Film Coated Carbon Nanotube Paste Electrode for the Determination of Curcumin with Vanillin: An Electroanalytical Approach

(**Monatshefte Fur Chemie/Chemical Monthly**, 151, 2020, 1681–1688. **IF: 1.45**)

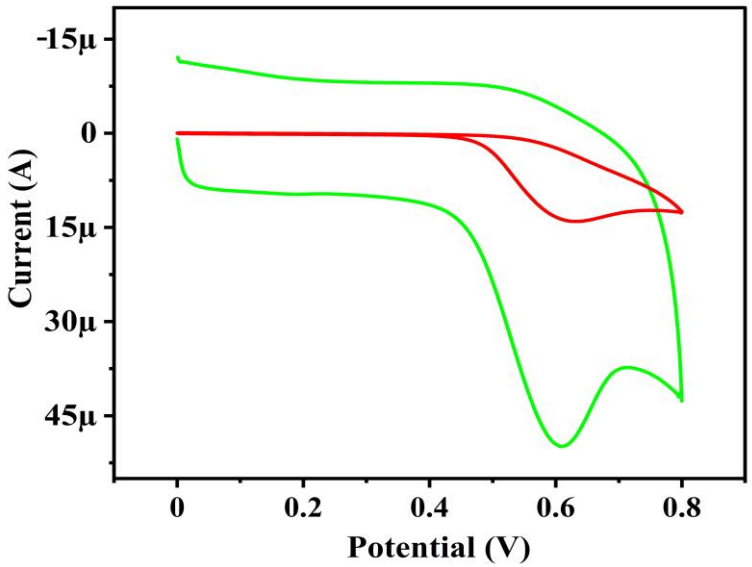
Poly (glutamine) film modified carbon nanotube paste electrode (PGAMCNTPE) was prepared through the electropolymerization technique. The prepared electrode was characterized by FE-SEM and electrochemical approaches. It was applied to electrochemical monitoring of CUR in PBS of pH 7.5 using CV and DPV. The BCNTPE was unable to identify CUR but PGAMCNTPE detects CUR oxidation at 0.168 V, and reduction at 0.098 V with good current sensitivity. Under calibrated Conditions, the PGAMCNTPE shows the linear voltammetric response from 0.4-6.0 and 6.0-10.0 µM for CUR, with the lower detection limit (DL) of 2.79×10^{-8} M. The planned CUR sensing strategy was applied to food supplement with excellent recovery from 90.0-97.0%. Also, a simultaneous determination was performed with VA with less interference- effect.



Chapter 7: Optimized Voltammetric Experiment for the Determination of Phloroglucinol at Surfactant Modified Carbon Nanotube Paste Electrode

(**Instruments and Experimental Techniques,** 63, 2019, 750-757. **IF: 0.57**)

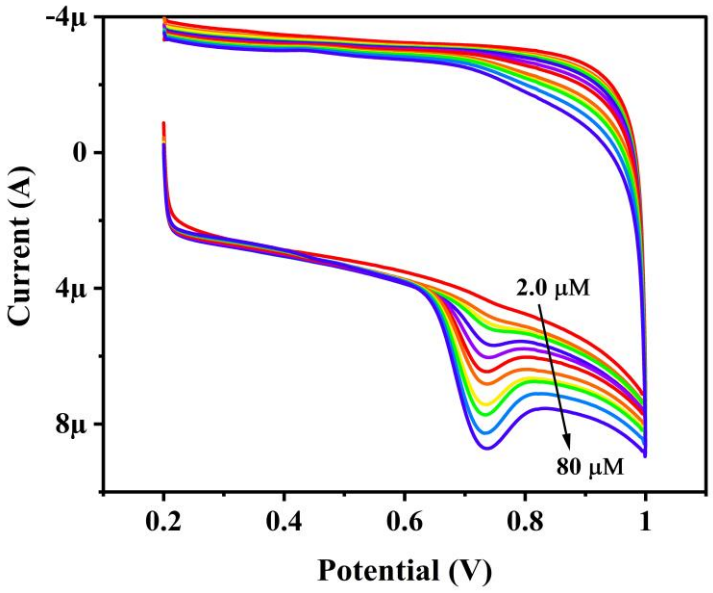
Present chapter describes the electrochemical of sensing and determination of phenolic compound (Phloroglucinol) using non-ionic surfactant Octyl phenol ethoxylate modified carbon nanotube paste electrode (OPEMCNTPE) in PBS (0.1 M, pH 6.0) by voltammetric method. The OPEMCNTPE was prepared by simple immobilization of microliters surfactant on the surface of the electrode. The developed electrode was characterized by FE-SEM and CV studies. The OPEMCNTPE shows an exceptional catalytic impact towards the electro-oxidation of Phloroglucinol (PL) in contrast to the BCNTPE. The rise in the concentration of PL is directly proportional to PL anodic peak current in the linear working range from 10.0 µM to 90.0 µM with a small detection limit (LOD) 0.71 µM. The proposed sensor provides good repeatability and stability. This method was utilized for the estimation of PL in the water and blood serum samples.



Chapter 8: Electrochemical Preparation of Poly (arginine) Modified Carbon Nanotube Paste Electrode and its Application for the Determination Pyridoxine in the Presence of Riboflavin: An Electroanalytical Approach

(**Journal of Analysis and Testing**, 3, 2019, 331-340.)

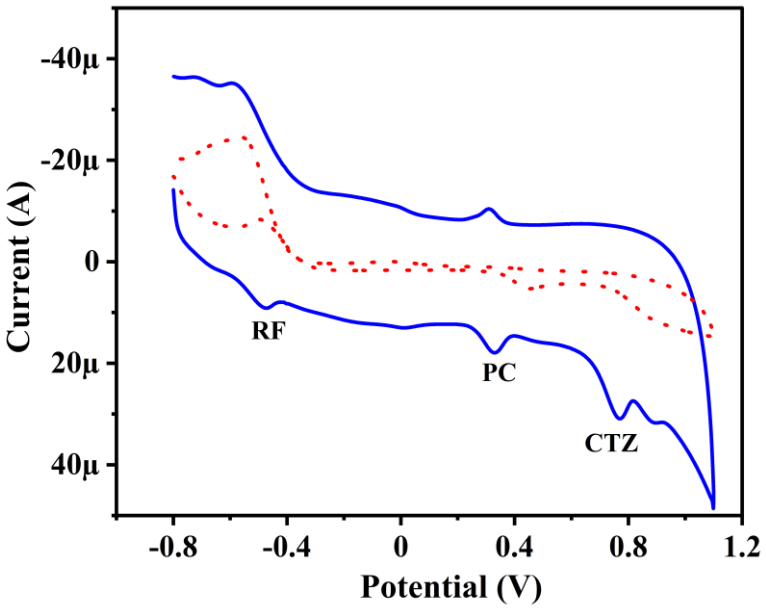
A simple poly (arginine) film-modified carbon nanotube paste electrode (PAMCNTPE) was prepared using CV. The sensor was subjected to FESEM and CV characterization. The sensing of 0.1 mM PY was upgraded at PAMCNTPE as compared to the BCNTPE. The PAMCNTPE detects the 0.1 mM PY at a specific potential 0.727 V with a current response of 10.68 μA. In the case of BCNTPE, the PY appeared at 0.798 V with a current of 2.90 μA. The proposed analytical method was optimized by prime parameters such as the impact scan rate, pH and PY concentration. Under optimal conditions, the concentration of PY is directly proportional to oxidation current (I_{pa}) in linear range 2.0–10.0 μM, and 10.0–80.0 μM with a LOD of 9.6×10^{-7} M and limit of quantification (LOQ) of 3.21×10^{-6} M. The proposed sensor was effectively applied for the determination of PY in natural food supplement with excellent recovery.



Chapter 9: Poly (DL-valine) Electro-Polymerized Carbon Nanotube Paste Sensor for the Determination of Antihistamine Drug Cetirizine

(**Journal of Electrochemical Science and Engineering,** 11, 2021, 27-38.)

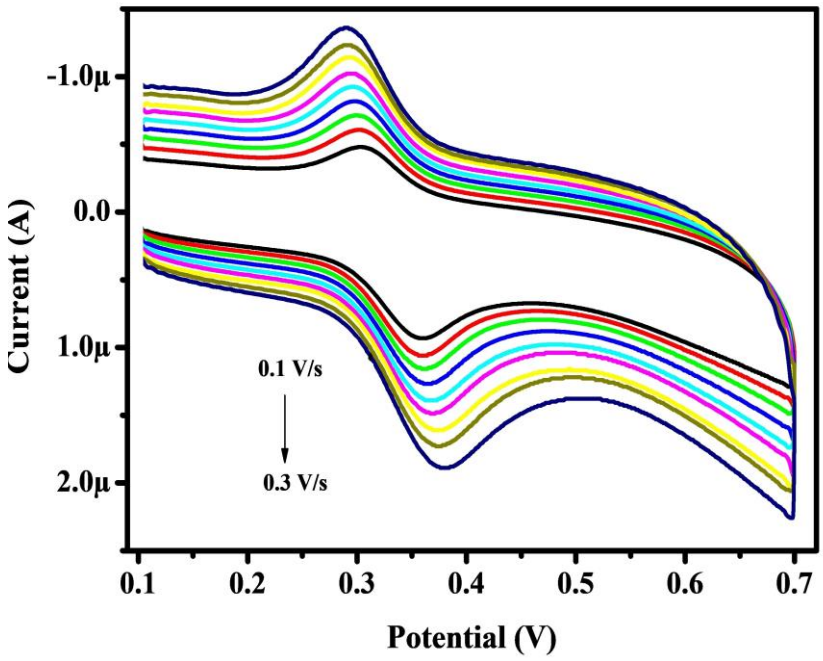
A disposable poly (DL-valine) modified carbon nanotube paste sensor (PVLMCNTPS) is prepared by electro polymerization route. The PVLMCNTPS and BCNTPS morphology was confirmed through FE-SEM and electrochemical studies. The optimized PVLMCNTPS was applied to improve the voltammetric determination of CTZ in 0.1 PBS of pH 6.5 using CV. The PVLMCNTPS surface composite creates electrocatalytic impact on oxidation CTZ as contrast to BCNTPS. The proposed PVLMCNTPS was calibrated using parameter such as accumulation time, number polymerization cycles, solution pH, voltage scan rate, effect of concentration etc. The PVLMCNTPS provides analytical linearity from 2.0 to 80 µM with detection limit (DL) 0.11 µM for CTZ determination. PVLMCNTPS is highly selective for CTZ in presence of interfering molecules. The stable and selective PVLMCNTPS was applied for CTZ determination in pharmaceutical pill with satisfactory results.



Chapter 10: Electrochemical Determination of Indigotine Based on Poly (Gibberellic Acid) Modified Carbon Nanotube Paste Electrode

(Book chapter accepted in: **Environment Applications of Carbon Nanomaterials-Based Devices,** https://doi.org/10.1002/9783527830978.ch5)

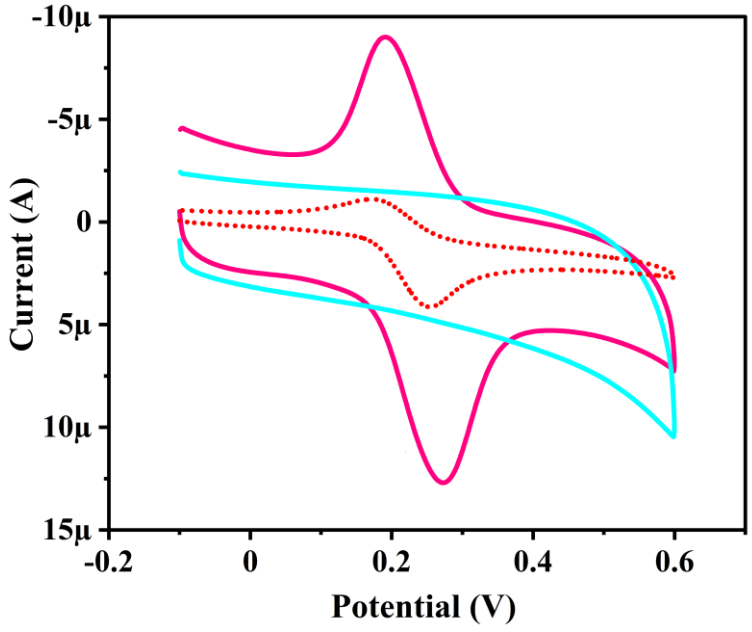
Herein, poly (gibberellic acid) film modified carbon nanotube paste electrode (PGAMCNTPE) was prepared by a rapid electropolymerization strategy. The prepared surface composite was characterized by FE-SEM, electrochemical impedance spectroscopy (EIS) and Voltammetric methods. Amplified electron transfer ability achieved at PGAMCNTPE as compared to BCNTPE. The stable and reproducible PGAMCNTPE was applied for the determination of IT which is eco-toxic. Under calibrated conditions, IT was determined by utilizing differential pulse voltammetry in the linear range 1.0-10.0 µM with the detection limit of 4.11×10^{-8} M. The analytical application of the proposed sensor was studied for estimation of IT in tap water using standard addition method.



Chapter 11. Electrochemistry Initiated Preparation of Poly (Riboflavin) Coated Graphite and Graphene Paste Electrode for the Quantification of Rutin in Presence of Hydroquinone

(Communicated to **Nature communications, I.F: 14.91**)

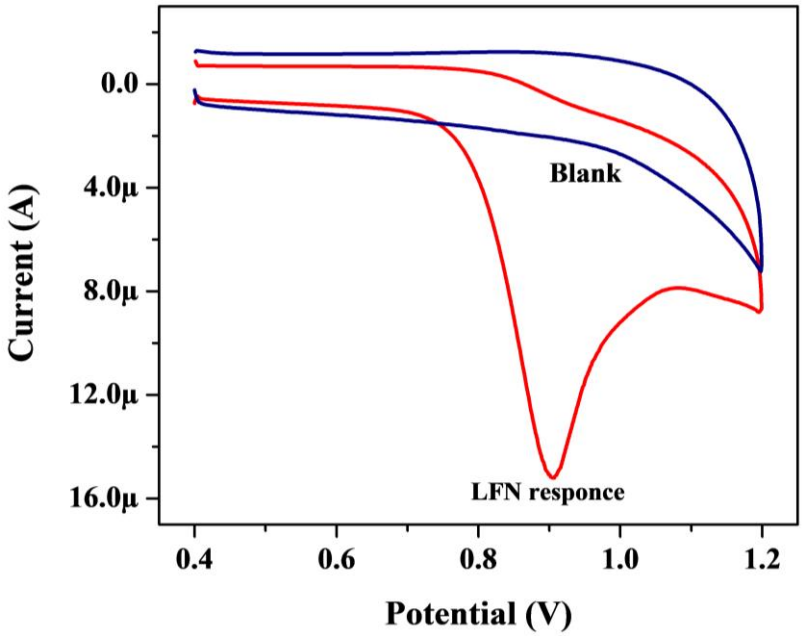
A poly (riboflavin) coated graphite paste surface composite was synthesized by effortless electrochemical polymerization method in stable pH 7.0 with 0.1 mM monomer in potential domain -1.0 to 1.5 V. The obtained poly (Riboflavin) coated graphite and graphene composite electrode (PRFGGCPE) and graphite graphene composite paste electrode (GGCPE) structural properties before and after modification are confirmed by FESEM, EDX, EIS, electrochemical characterization. PRFGGCPE delivers upsurge electrochemical responses with quasi reversibility but in case GGCPE, it shows low binding ability and low current response for RU with deviation from quasi reversibility. Under optimized analytical criteria, PRFCGPE detects RU in the range 1.0-10.0 with impressive detection limit of 46.2 nM. The real time RU testing is performed in green tea sample with satisfactory recoveries with low matrix effect.



Chapter: 12. Electrochemical Determination of Levofloxacin at Poly (Clayton Yellow) Treated Carbon Paste electrode

(Communicated to **Chemical Data Collections**)

An effortless and quick analytical method was proposed for determination of Levofloxacin (LFN) at poly (Clayton yellow) treated carbon paste electrode (PCYTCPE). The proposed PCYTCPE and untreated carbon paste electrode (UTCPE) were characterized by field emission scanning microscope (FESEM), energy dispersive X ray spectroscopy (EDX), and electrochemical characterization. It generates clear and intense peak for LFN (0.1 mM) by regulating over-potential as compared to UTCPE. Under optimized conditions, DPV was applied for LFN in rage 0.1 µM to 1.0 µM with a low detection limits. Finally real-time analysis was performed in blood serum samples with excellent recovery.



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LIST OF PUBLICATIONS

1. **Girish Tigari,** J. G. Manjunatha**,** A Surfactant Enhanced Novel Pencil graphite and Carbon Nanotube Composite Paste Material as an Effective Electrochemical Sensor for Determination of Riboflavin, **Journal of Science: Advanced Materials and Devices** 5, 2020, 56-64. **I.F: 5.46**

2. **Girish Tigari,** J. G. Manjunatha**,** Surfactant and Polymer Composite Modified Electrode for the Sensitive Determination of Vanillin in Food Sample, **ChemistrySelect** 6, 2021, 2700-2708. **I.F: 2.109**

3. **Girish Tigari,** J.G. Manjunatha, C. Raril, N. Hareesha, Determination of Riboflavin at Carbon Nanotube Paste Electrodes Modified with an Anionic Surfactant, **Chemistry Select**, 4, 2019, 2168 -2173. **I.F: 2.109**

4. **Girish Tigari,** J. G. Manjunatha, Poly (glutamine) Film Coated Carbon Nanotube Paste Electrode for Determination of Curcumin with Vanillin: An Electroanalytical Approach. **Monatshefte Fur Chemie/Chemical Monthly**, 151, 2020, 1681-1688. **IF: 1.45**

5. **Girish Tigari,** J. G. Manjunatha, Optimized Voltammetric Experiment for the Determination of Phloroglucinol at Surfactant Modified Carbon Nanotube Paste Electrode, **Instruments and Experimental Techniques,** 63, 2019, 750-757. **IF: 0.57**)

6. **Girish Tigari**, J. G. Manjunatha, Electrochemical Preparation of Poly (arginine) Modified Carbon Nanotube Paste Electrode and its Application for the Determination Pyridoxine in the Presence of Riboflavin: An Electroanalytical Approach, **Journal of Analysis and Testing**, 3, 2019, 331-340.

7. **Girish Tigari,** J. G. Manjunatha, Poly (DL-valine) Electro-Polymerized Carbon Nanotube Paste Sensor for the Determination of Antihistamine Drug Cetirizine, **Journal of Electrochemical Science and Engineering**, 11, 2020, 27-38. **CiteScore: 1.7**

8. **Girish Tigari**, J. G. Manjunatha, Electrochemical Determination of Indigotine Based on Poly (Gibberellic Acid) Modified Carbon Nanotube Paste Electrode, Accepted in book: **Environment Applications of Carbon Nanomaterials-Based Devices.** doi: 10.1002/9783527830978.ch5

9. **Girish Tigari**, J. G. Manjunatha, Enhanced Electrochemical Determination of Riboflavin in Biological and Pharmaceutical Samples At Poly (Arginine) Modified Carbon Paste Electrode, **Methods Objects of Chemical Analysis** 14, 2019, 216-223.

10. **Girish Tigari**, J. G. Manjunatha, Electrochemical Determination of Resorcinol with Tartrazine at Non-Ionic Surfactant Modified Graphite Powder and Carbon Nanotube Composite Paste Electrode, **Novel Approaches in Drug Design and Development** 4, 2019, 555647.

11. C. Raril, J. G. Manjunatha, **Girish Tigari**, Low-cost voltammetric sensor based on an anionic surfactant modified carbon nanocomposite material for the rapid determination of curcumin in natural food supplement, **Instrumentation Science & Technology**, 48, 2020, 561-582. **I.F: 1.58.**

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13. N. Hareesha, J. G. Manjunatha, C. Raril, **Girish Tigari**, Design of novel Surfactant Modified Carbon Nanotube Paste Electrochemical Sensor for the Sensitive Investigation of Tyrosine as a Pharmaceutical Drug, **Advanced Pharmaceutical Bulletin**, 2019, 9, 132-137. **Cite Score: 4.8**

14. P.A. Pushpanjali, J. G. Manjunatha, **Girish Tigari**, S. Fattepur, Poly (Niacin) Based Carbon Nanotube Sensor for the Sensitive and Selective Voltammetric Detection of Vanillin with Caffeine, **Analytical Bioanalytical Electrochemistry**, 12, 2020, 553-568. **CiteScore: 1.38**

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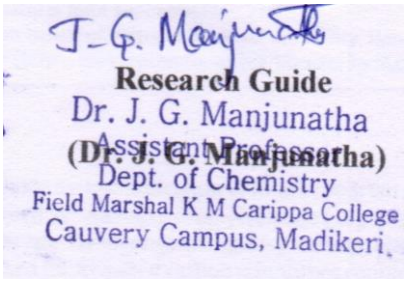

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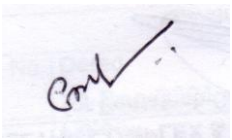

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Original Article

A surfactant enhanced novel pencil graphite and carbon nanotube composite paste material as an effective electrochemical sensor for determination of riboflavin

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ABSTRACT

A novel sensor fabrication using anionic surfactant sodium lauryl sulphate modified carbonnanotube and pencil graphite composite paste electrode (SLSMCNTPGCPE) is prepared and characterized using Field Emission Scanning Electron Microscope (FE-SEM) and Cyclic Voltammetry (CV). The devised SLSMCNTPGCPE is a responsive electrode material for the determination of Riboflavin (RF) as compared to carbon nanotube and pencil graphite composite paste electrode (CNTPGCPE) and bare pencil graphite paste electrode (BPGPE). The fabricated sensor shows a linear current response to a diverse concentration of RF in 0.2–0.8 μM and 1–5 μM with a low detection limit of 1.16×10^{-8} M by applying differential pulse voltammetry (DPV). The stability, reproducibility, repeatability, interference and concurrent investigation with dopamine (DA) have been done with satisfactory outcomes. The new sensor was applied for the RF estimation shows good recovery in B-complex pill and natural food supplement.

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1. Introduction

Vitamins and neurotransmitters are biologically active molecules and play a vital role in the humanoid biochemistry and metabolism. RF (vitamin B_2) is aqueous soluble and a principal component of flavoenzymes. It assists the conversion of carbohydrates, fats, and proteins into energy and supports the body during anxiety [1–3]. RF cannot be formed in the human body, so it has to be obtained from nutritional sources such as milk, eggs, green vegetables, tea, wine, liver, etc. The lack of RF in the human body may lead to eye and skin disorders [4–6]. Dopamine (DA) is a neurotransmitter molecule in the mammalian central nervous system and plays a substantial role in operating the central nervous, hormonal, renal and cardiac systems. Abnormal levels of DA in the human brain cause brain diseases, such as Parkinson's and Schizophrenia [7–13].

RF is determined using different analytical procedures such as high-performance liquid chromatography [14], spectrophotometry [15], Flow injection analysis [16], mass spectrometry [17], etc. These analytical techniques are expensive and time-consuming. Also, some voltammetric methods for quantification of RF are reported in the previous literature such as: mercury drop electrode [18], ZnO/Manganese hexacyanoferrate nanocomposite/glassy carbon electrode [19], Highly dispersed multiwalled carbon nanotubes coupled manganese salen nanostructure [20], pre-treated GC [21], Manganese (III) Tetraphenyl porphyrin Modified Carbon Paste Electrode [22], pencil graphite [23], Reduced graphene oxide [24], Poly (3-methyl thiophene) Modified Glassy Carbon Electrode [25], etc.

Electroanalytical approaches are active and gifted analytical practices having a strong impact on human health and environmental monitoring. The electrochemical methods are strongly recognized due to low cost, simple preparations, rapid analyzing time with the outstanding analytical performance [26–32]. Pencil graphite is known to be a multipurpose tool for electroanalysis of bioactive molecules due to their sp^2 hybridized carbon which shows characteristics like excellent electrical conductivity, adsorption, little background current, easy exterior modification and mechanical stability [33–35]. Carbon nanotubes (CNTs) are frequently used in the fabrication of electrochemical sensors due to their excellent electronic properties, rapid renewal, extensive potential ranges, less residual noise with extreme stability [36–38]. Surfactants (SDS, TX-100, CTAB), nanomaterials, stainless steel powder, ferrocene, etc can alter and regulate the characteristic properties of electrode surfaces, which leads to changes in the

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Analytical Chemistry

Surfactant and Polymer Composite Modified Electrode for the Sensitive Determination of Vanillin in Food Samples

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In this work, the active poly (titan yellow) and octoxynol-9 modified carbon nanotube paste electrode (PTOMCNPE) was prepared and characterized through a Field emission scanning electron microscope (FE-SEM), Energy-dispersive X-ray Spectroscopy (EDX), and Electrochemical Impedance Spectroscopy (EIS). It promotes the detection and quantification of vanillin (VA). The electrochemical parameters such as the number of electropolymerization cycles, effect of surfactant amounts, influence of pH, and scan rate were optimized to get an enhanced current signal for the targeted molecule. Under calibrated conditions, the concentration linearity for vanillin was 2.0-40.0 μM using both cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The detection limit (LOD) for determination VA was found to be 4.9×10^{-8} M and 9.31×10^{-8} M using DPV and CV respectively. The stable and selective sensor was applied to food samples with excellent recovery.

1. Introduction

VA is widely used as a flavouring agent in food, beverages, perfumes, pharmaceutical products, etc. The intake of VA has both benefits and adverse effects on human health. VA intake is beneficial for heart and anemia patients, but an overdose of VA (above 10 mg kg^{-1}) can trigger problems like headaches, vomiting, nausea and affects kidney, and liver functioning.[1–4] Therefore, a robust analytical method for the quantification of VA is important. Different analytical methods were reported previously for the estimation of VA, such as HPLC,[5] spectrophotometry,[6] GC-MS,[7] etc. But these techniques demand more time, cost, consumes more solvents and reagents, also require experts for handling.

Electroanalytical methods are better alternatives and widely used analytical methods for monitoring bioactive molecules in clinical, food, environmental, pharmaceutical samples because they are quick, relatively low cost and provide low detection limits with high sensitivity.[8–10] Previously electrochemical sensors were developed for the detection and quantification of VA such as acetylene black paste electrode modified with graphene-poly vinylpyrrolidone composite film,[11] graphene nano-flakes modified glassy carbon electrode,[12] manganese dioxide-graphene composite,[13] screen-printed electrode,[14] Au–Ag alloy nanoparticles,[15] etc.

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Carbon nanotubes were repeatedly used for the preparation of voltammetric sensors due to their extreme stability, extensive potential window, high adsorption capability, low background current.[16–19] Electro-polymerization and surfactant immobilization are two different techniques used for improving electrode sensing performance. These techniques were commonly used for the surface modification of electrodes because the surfactant drop and polymer layered electrode give an enhanced electrocatalytic effect by controlling over potential.[20–22] In the present work electrochemical methodology was developed for the determination of VA in food samples. For this goal, PTOMCNPE was prepared by electropolymerization and surfactant immobilization techniques. The prepared composite material shows an enhanced electrocatalytic effect for the electro-oxidation of vanillin and It is efficient for detection of VA in presence of folic acid (FA), curcumin (CRC), ascorbic acid (AA). To the best of knowledge, there no electrochemical sensor-based poly (titan yellow) and octoxynol-9 modified carbon nanotube paste electrode for VA.

2. Results and discussion

2.1. Fabrication of PTOMCNPE and optimization

PTOMCNPE was performed by running continuous cycles from potential 0.0–1.4 V in an electrochemical cell containing 0.1 mM titan yellow with 0.1 M PBS of pH 7.0. It can be seen from Figure 1. A as the cyclic time increases the titan yellow curves were descended. This shows the polymer layers of titan yellow were formed on the surface of the carbon nanotube paste material. The prepared electrode was rinsed with distilled water to erase the unreacted monomer. Ten polymerization scans were optimized for sensing VA (Figure 1B). The prepared poly (titan yellow) modified carbon nanotube paste material is further modified by octoxynol-9 immobilization. The surfactant amount was also optimized for the detection of VA (0.5×10^{-4} M). Surfactant concentration varied from 5.0–20 μL and

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Analytical Chemistry

Determination of Riboflavin at Carbon Nanotube Paste Electrodes Modified with an Anionic Surfactant

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A Sodium lauryl sulfate modified carbon nanotube paste electrode (SLSMCNTPE) was fabricated for the electroanalysis of Riboflavin (RF) in phosphate buffer solution (PBS) at pH, 7.0 by cyclic voltammetry (CV). The electrode was found to be a very sensitive tool for detection of RF; it was shown that SLSMCNTPE yields a high current response towards RF as compared to the bare carbon nanotube paste electrode (BCNTPE). Key parameters were optimized for RF determination. The effects of surfactant concentration, pH, scan rate and concentration of RF on the oxidation peak current values were determined. The RF oxidation peak appeared at −440 mV and reduction peak at −575 mV vs. saturated calomel electrode (SCE). The SLSMCNTPE revealed good repeatability, reproducibility, stability, high electrochemical sensitivity in its voltammetric response and a detection limit of 9.25×10-8 M.

Introduction

RF or vitamin B_2 is a water soluble vitamin and an essential constituent of flavoenzymes which plays a vital role in biochemical reactions of the human body. It cannot produce in the human body hence has to be gained dietary from the sources such as liver, cheese, milk, meat, eggs, wines, and tea. Its deficiency is accompanying eye problems and skin disorders.[1–3]

RF was routinely determined by means of spectrophotometry,[4] UHPLC/LC–MS,[5] chemiluminescence,[6] and liquid chromatography-diode array detection (LC–DAD).[7] These are expensive and time-consuming approaches. Also, some electroanalytical technique were established using silica gel modified zirconium oxide electrode,[8] adsorptive cathodic stripping voltammetry at hanging mercury drop electrode,[9] silver solid amalgam electrode,[10] polythiophene nanotube arrays,[11] bismuth film electrode.[12]

Electrochemical techniques are versatile and powerful tools for the analysis of biological molecules, assay of pharmaceutical drugs, food analysis, and medical diagnosis. The electrochemical techniques have great attention due to their simple preparation, sensitivity selectivity, and low cost, rapid response time. The usage of chemically modified electrodes offers a tool for boosting the detection capacity of electrodes and various functional materials are used as a modifier for the fabrication of electrochemical sensors.[13–20]

A carbon nanotube paste electrode (CNTPE) was repeatedly utilized for the construction of biosensors. Due to their excellent electrical, mechanical properties, low residual current and noise, rapid surface renewal, wide anodic and cathodic potential ranges. There were previously conveyed plentiful carbon electrodes and modifiers such as SDS, TX-100, poly-(glycine), poly-(N, N-dimethylaniline), silica gel, and glucose, nanoparticles. Which were found to be extremely sensitive to acids and basis media. The drive of these modifiers is due to the reducing over potential for the reduction/oxidation of analytes in contrast with the unmodified electrode.[21–35] The Objective of the current study is that carbon nanotube paste electrode modified with SLS for voltammetric determination of the RF with wavering parameters like scan rate, pH, and concentration in 0.2 M PBS (pH 7.0). To best of our information, there was no voltammetric sensor based on SLSMCNTPE for the determination of RF.

Results and Discussion

FESEM profile of BCNTPE and SLSMCNTPE

Figure 1. Illustrates the FESEM images of BCNTPE (Figure 1a) and SLSMCNTPE (Figure 1b) surfaces. The FESEM image of BCNTPE displays an irregular morphology on the electrode surface. Whereas the FESEM images of SLSMCNTPE show an agglomerated morphology, which specifies the electrode was well modified with SLS.

Optimization of SLS

In this section, the effect of the amount of SLS (5-20 μL) on the RF anodic peak currents is studied by CV. As shown in Figure 2. The anodic peak current was −136.9 μA for 10 μL SLS, so it was highly sensitive for 10 μL SLS, for other amounts it was less sensitive. It clearly indicates the critical aggregation concentration (CAC) was reached at 10 μL of SLS (25×10^{-3} M) further increase in the amount of SLS the peak current decreases. Therefore 10 μL was agreed for modification of CNTPE to carry out the whole experiment. We can say the surfactant amount

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ORIGINAL PAPER

Poly(glutamine) film-coated carbon nanotube paste electrode for the determination of curcumin with vanillin: an electroanalytical approach

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Abstract
Poly(glutamine) film-modified carbon nanotube paste electrode (PGAMCNTPE) was prepared through the electropolymerization technique. The prepared electrode was characterized by Field Emission Scanning Electron Microscope (FE-SEM) and electrochemical approaches. It was applied to electrochemical monitoring of curcumin in phosphate buffer of pH 7.5 using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The bare carbon nanotube paste electrode was unable to identify curcumin, but PGAMCNTPE detects curcumin oxidation at 0.168 V and reduction at 0.098 V with good current sensitivity. Under calibrated conditions, the PGAMCNTPE shows the linear voltammetric response from 0.4 to 6 and 6 to 10 µM for curcumin, with the lower detection limit of 2.79×10^{-8} M. The planned curcumin sensing strategy was applied to food supplement with excellent recovery from 90 to 97%. Also, a simultaneous determination was performed with vanillin with less interference effect.

Graphic abstract

Keywords Poly(glutamine) · Carbon nanotube paste · Curcumin · Voltammetry · Electron transfer · Cyclic voltammetry · Biosensors

Introduction

Curcumin (CUR) is a yellow-colored phenolic substance naturally obtained from the rhizome of *Curcuma longa*. CUR is widely used as a food additive and coloring agent [1, 2]. It has potential medicinal properties such as antibacterial, anti-inflammatory, anti-tumor, anti-ischemic, and immunomodulatory with non-toxic nature. CUR is used as a drug in the treatment of Alzheimer's, sclerosis and dementia disorders [3–5]. Therefore, it is essential to develop a quantization method for CUR molecules. Previously, a variety of analytical strategies were reported such as capillary electrophoresis [6], chromatography [7], spectroscopic method [8], fluorimetric analysis [9], and electroanalytical methods [10–15]. Among versatile analytical approaches, electroanalytical strategies are fascinating and popular analytical tools due to exceptional benefits such as low cost, quick analyzing capacity, and high sensitivity with the exceptional analytical applicability in analyzing bioactive molecules in complicated matrices such as biological, pharmaceutical, environmental, and food samples [16–34].

Electropolymerization is a frequently used voltammetric tool to synthesize thin film on an electrode. Previously, many polymer-coated surfaces were reported as

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PHYSICAL INSTRUMENTS FOR ECOLOGY, MEDICINE, AND BIOLOGY

Optimized Voltammetric Experiment for the Determination of Phloroglucinol at Surfactant Modified Carbon Nanotube Paste Electrode

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Abstract—Present work describes the electrochemical sensing and determination of phenolic compound (Phloroglucinol) using non-ionic surfactant Octyl phenol ethoxylate modified carbon nanotube paste electrode (OPEMCNTPE) in PBS (0.1 mol, pH 6.0) by Voltammetric method. The developed electrode was characterized by field emission scanning electron microscope (FE-SEM) and cyclic voltammetric (CV) studies. The OPEMCNTPE shows an exceptional catalytic impact towards the electro-oxidation of Phloroglucinol (PL) in contrast to the bare carbon nanotube paste electrode (BCNTPE). The rise in the concentration of PL is directly proportional to PL anodic peak current in the linear working range 10–90 μmol with a small detection limit (LOD) 0.71 μmol. This method was utilized for the estimation of PL in the water and blood serum samples.

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INTRODUCTION

Phloroglucinol (PL) $C_6H_3(OH)_3$ is an essential colourless phenolic substance that naturally occurs in plants. It is used in the production of explosives and pharmaceuticals. It has important medicinal value due to its antispasmodic action with less toxicity. It is also a reagent in lignin, vanillin, and pentose analysis. Overdose of PL causes adverse effects such as vomiting, ataxia, cyanosis, coma and choking. It is also destructive to the environment [1–7]. Hence, it is important to detect and trace the amount of PL. Existing methods in analysing PL such as chemiluminescence, high-performance liquid chromatography (HPLC/MS), and thin-layer chromatography, ion chromatography [8–11], etc are time-consuming and costly techniques. Few electroanalytical methods were also reported previously such as graphene oxide and iron hydroxide colloid modified glassy carbon electrode [12], ZnO—N-(tri methoxy silyl propyl) ethylenediamine tri acetic acid modified glassy carbon electrode [13] Surfactant/MWCNTS/Glassy carbon [14].

Carbon nanotubes are frequently used in electroanalysis of bioactive molecules due to their unique properties such as low background current, long potential domains, high electric conductivity, compatibility, stability, and easy surface modification, etc. [15–20]. The surfactants (cationic, anionic and non-ionic) are the substances that reduce the surface tension between the solid-solution interfaces and enhance the electrochemical sensing properties of the electrode [21–25]. In this paper an active electrochemical sensor is fabricated based on the octyl phenol ethoxylate modified carbon nanotube paste electrode. To the best of our information, no voltammetry sensor was prepared based on octyl phenol ethoxylate modified carbon nanotube paste electrode for the detection of PL.

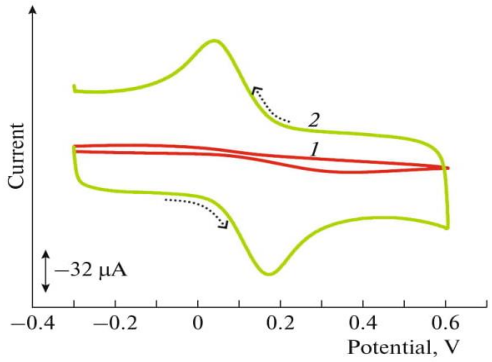

Fig. 1. Electroanalytical characterization of BCNTPE (curve *1*) and OPEMCNTPE (curve *2*) using standard 1 mmol $K_4[Fe(CN)_6]$.

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ORIGINAL PAPER

Electrochemical Preparation of Poly(arginine)-Modified Carbon Nanotube Paste Electrode and its Application for the Determination of Pyridoxine in the Presence of Riboflavin: An Electroanalytical Approach

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Abstract
A simple poly(arginine) film-modified carbon nanotube paste electrode (PAMCNTPE) was prepared using cyclic voltammetry (CV). The devised sensor was subjected to field-emission scanning electron microscope (FESEM) and CV characterization. The sensing of 0.1 mM pyridoxine (PY) was upgraded at PAMCNTPE as compared to the bare carbon nanotube paste electrode (BCNTPE). The PAMCNTPE detects the 0.1 mM PY at a specific potential 0.727 V with a current response of 10.68 µA. In the case of BCNTPE, the PY appeared at 0.798 V with a current 2.90 µA. The proposed analytical method was optimized by prime parameters such as the impact scan rate, pH and PY concentration. Under optimal conditions, the concentration of PY is directly proportional to oxidation current (I_{pa}) in linear range 2–10 µM, and 10–80 µM with a detection limit (LOD) of 9.6×10^{-7} M and limit of quantification (LOQ) of 3.21×10^{-6} M. The simultaneous determination, concentration variation analysis of PY is performed with riboflavin (RF) and interference analysis in detecting PY also examined. The proposed sensor was effectively applied for the determination of PY in natural food supplement with excellent recovery.

Keywords Poly(arginine) · Carbon nanotube · Pyridoxine · Riboflavin · Cyclic voltammetry

1 Introduction

PY (vitamin B_6) is an aqueous soluble B-vitamin, and it is involved in human metabolism and biochemical reactions. PY is required for the human body to maintain physical and psychological health. It is having a significant role in the synthesis of noradrenaline, dopamine, serotonin, and histamine in the human body. It is involved in the production of red blood cells (RBC) and reduces the risk of colorectal cancer. It acts as a coenzyme for many enzymatic reactions. Its inadequacy causes neurological and skin disorders [1–5]. RF (vitamin B_2) belongs to B-group of vitamins which are found in an egg, meat, liver, and milk as a micronutrient. It is essential for the human body. Lack of RF in the human body causes skin and eye problems. These B-vitamins play a substantial role in human biochemistry; thus, it is necessary to develop a simple and quick analytical method for the determination of PY and RF [6–8]. There were previously reported a variety of analytical techniques such as chromatography, spectrophotometry, fluorescence spectroscopy [9–11], etc. However, these methods are costly and time-consuming analytical methods. The best substitute for the above methods are electroanalytical approaches like mesoporous TiO_2 and SnO_2 nanocatalyst-modified glassy carbon electrode, cobalt hexacyanoferrate-modified carbon paste electrode, carbon paste electrode modified with crown ethers, multi-wall carbon nanotube-modified carbon-ceramic electrode, copper nanoparticle-modified polycrystalline gold electrode, platinum electrode, electro-deposition of gold nanostructure-modified carbon paste electrode, etc. [12–18].

In sensor fabrication, the carbon nanotubes (CNTs) were frequently used due to their characteristic properties such as high electrical conduction, extreme stability, low noise, long voltage domains, and easy renewability [19, 20]. The polymeric films such as poly(glycine), poly(nigrosine), poly(methyl Orange), poly(rosaniline), solid R, etc. were used for the voltammetric analysis of biomolecules, because

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Original scientific paper

Poly (DL-valine) electro-polymerized carbon nanotube paste sensor for determination of antihistamine drug cetirizine

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Abstract

Poly (DL-valine) modified multiwalled carbon nanotube paste sensor (PVLMCNTPS) was prepared by electro-polymerization route. PVLMCNTPS and bare multiwalled carbon nanotube paste sensor (BMCNTPS) morphologies and sensing properties for cetirizine (CTZ) were confirmed through a field emission scanning electron microscope (FE-SEM) and electrochemical studies, respectively. In contrast to BMCNTPS, PVLMCNTPS surface composite creates an electrocatalytic impact on the oxidation of CTZ. PVLMCNTPS properties were optimized using parameters such as accumulation time, number of polymerization cycles, solution pH, and scan rate. The optimized PVLMCNTPS was applied for the determination of cetirizine in 0.1 M phosphate buffer solution (PBS) of pH 7.0, using cyclic voltammetry (CV). It is shown that PVLMCNTPS provides analytical linearity from 2.0 to 80 µM, with detection limit of 0.11 µM for CTZ determination. PVLMCNTPS was found highly selective for CTZ in presence of some interfering organic molecules. The stable and selective PVLMCNTPS was applied for CTZ determination in pharmaceutical pills with satisfactory results.

Keywords

Polymer modified sensor; drug analysis; cyclic voltammetry

Introduction

Cetirizine (CTZ) is an antihistamine drug which is usually prescribed for allergic symptoms like running nose, itching, hives, watery eyes, body ache, *etc*. It acts as an allergy reliever by blocking

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Enhanced Electrochemical Determination of Riboflavin in Biological and Pharmaceutical samples at Poly (Arginine) Modified Carbon Paste Electrode

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An electrogenerated Polyarginine modified carbon paste electrode (PAMCPE) was fabricated through a simple electropolymerization procedure. The devised electrode was characterized by cyclic voltammetry (CV) and Field Emission Scanning Electron Microscopy (FESEM). The equipped PAMCPE was implemented to the electrocatalytic estimation of Riboflavin (RF) and its instantaneous resolution with ascorbic acid (AA) and folic acid (FA) in phosphate buffer solution (PBS) of pH 6.0 by differential pulse voltammetry (DPV). It was originated to be an extremely responsive and choosy approach for the electrochemical detection and quantification of RF. It was revealed that PAMCPE generates higher current response towards RF contrast to the bare carbon paste electrode (BCPE). Under optimized condition, the RF oxidation current values were linearly reliant on the RF concentration increment with a limit of detection (LOD) of $9.3 \cdot 10^{-8}$ M using DPV. The stable PAMCPE was effectively executed for estimation of RF in B-complex pill and complex human blood serum samples.

Keywords: electrochemical sensor, poly(arginine), carbon paste electrode, vitamin B_2, human blood serum, B-complex capsule

The vitamins are bioactive species which plays a substantial role in human metabolic pathways. Riboflavin (vitamin B_2) is water-soluble, the major constituent of flavoenzymes which plays a crucial role in the biochemistry of the human body. It cannot be formed in the humanoid body; thus, it has to be attained through diet from the food sources such as milk, egg, vegetables, mushrooms, almonds and meat. Its inadequacy causes eye and skin problems. [1-4]. Ascorbic acid (AA) is water-soluble vitamin (Vitamin C), and it is found in foodstuffs, fruits, and which is used as a dietary supplement. Its deficiency is associated with a disease called scurvy. The AA is frequently used as an antioxidant in food, pharmaceutical formulations, and cosmetic applications and it is also useful in cancer impediment and immunity enrichment [5-9]. Folic acid (FA) is also known as folate (vitamin B_9), found in leafy vegetables, pasta, bread, liver, its deficiency causes anemia, and it is utilized in the treatment of stroke, ischaemic heart attack, cancer, liver diseases [10-13].

Vitamins were determined concurrently and independently by dissimilar methods such as Fluorescence[14], spectrophotometry[15], spectro-flurometry[16], high performance - diode array detection[17], reverse phase HPLC [18], these are expensive and time-consuming approaches, also a few of electrochemical methods reported for simultaneous and individual determination of vitamins such as conducting polymer modified glassy carbon electrode [19], Metallic Bulk Annular Band Electrodes [20], silver doped poly (arginine) modified glassy carbon electrode [21], hydroquinone derivative multiwall carbon nanotube paste electrode [22], screen printed carbon sensor [23] etc.

Electroanalytical practices are flexible and superior tools for the biomolecular and clinical diagnosis. The electrochemical procedures are established in great curiosity due to their effortless preparation, sensitivity, selectivity, and low cost, swift response time [24-30]. The implication of surface-modified electrodes is a strategy for enhancing the sensing efficiency of electrodes. The variety of functional molecules are employed as a modifier for the production of biosensors. The carbon materials bearing an exceptional electrical and mechanical feature so they are recurrently used in the construction of biosensors [31-33]. The modifiers such as TX -100, SDS, CTAB, CPC etc, (surfactants), conducting polymeric films, nanomaterials, ionic liquids etc. were used to regulate over potential and to accelerate the sensing property of electrode [34-35]. The goal of present work is the fabrication of a responsive and selective voltammetric sensor based on poly (arginine) modified carbon paste for voltammetric determination of RF in the existence of AA, and FA.

Novel Approaches in Drug Designing & Development

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Electrochemical Determination of Resorcinol with Tartrazine at Non-Ionic Surfactant Modified Graphite Powder and Carbon Nanotube Composite Paste Electrode

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Abstract

In this study, a sensitive and selective electrochemical sensor was developed for electrochemical determination of resorcinol (RC) using graphite powder and carbon nanotube composite paste electrode modified with TX-100 (TX-100/GPCNTCPE) in phosphate buffer solution (PBS), pH 7.0 using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The GPCNTCPE/TX-100 gives excellent current response for resorcinol as compared to bare graphite powder and carbon nanotube composite paste electrode (BGPCNTCPE). The impact of pH, Sweep rate and concentration of RC were evaluated. The anodic peak of RC was detected at 0.503 V vs. SCE with current response 11.40 μA. The proposed sensor offers low detection limit of order 3.41×10^{-6} M and limit of quantization (LOQ) is 11.42×10^{-6} M . This sensor is also adopted for simultaneous determination RC and tartrazine (TZ).

Keywords: Carbon Nanotubes; TX-100, Resorcinol; Electrochemical Determination; Tartrazine

Introduction

RC (Benzene-1, 3-diol) is a phenolic organic compound with high toxicity can cause dermatitis, catarrh, convulsion, cyanopathy, and even death. It has excellent medicinal value in treating skin disorders like Acne, seborrhoea dermatitis, eczema, psoriasis, and other skin infection. It is also used as a hair colouring agent, antiseptic and disinfectant [1-3]. So, it is too essential to detect and quantify the resorcinol. There were various methods reported regarding the estimation of RC such as Fluorescence [4] high- performance liquid chromatography [5] flow injection chemiluminescence [6] surface Plasmon resonance [7], but these are costly and time-consuming approaches. Also, some electrochemical methods were reported for the detection of resorcinol, the electrochemical methods were established due to its rapid sensitivity and low cost. SDS, TX-100, CTAB and polymer film Modified Carbon nanotubes (CNTs) and graphite paste electrode are wildly used in the electrochemical determination of vitamins, drugs, hormones, neurotransmitters, and food dyes [8-16], etc. due to their high mechanical strength and good electro-conductive property [17]. In this work graphite powder carbon nanotube composite paste modified with TX-100 is fabricated for voltammetric determination of RC and its simultaneous resolution with TZ. To the best of our knowledge, no voltammetric sensor built for concurrent resolution of RC with TZ based on TX-100/GPCNTCPE. The oxidation Process of RC is shown in Figure 1.

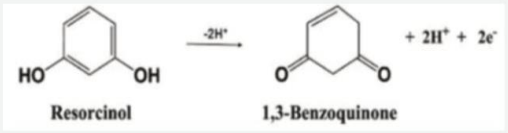

Figure 1: Oxidation process of RC.

Materials and Methods

Apparatus

The CV and DPV were obtained by means of CHI-6038E electrochemical analyzer in combination with a typical three-electrode system and a personal computer for data storage and processing. The GPCNTCPE and TX-100/GPCNTCPE was used as the working electrode, saturated calomel electrode (SCE) and a platinum wire were used as a reference electrode and auxiliary

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Low-cost voltammetric sensor based on an anionic surfactant modified carbon nanocomposite material for the rapid determination of curcumin in natural food supplement

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ABSTRACT

A highly sensitive and selective voltammetric method was developed for the determination of curcumin using sodium dodecyl sulfate modified carbon nanocomposite paste electrode. The electrochemical performance for curcumin was characterized by the use of linear sweep voltammetry, cyclic voltammetry, and differential pulse voltammetry. These measurements showed that the sodium dodecyl sulfate modified carbon nanocomposite paste electrode provided excellent electrocatalytic enhancement for the oxidation of curcumin compared to an unmodified carbon nanocomposite paste electrode. Using the optimized conditions, the oxidation peak current showed a linear response from 2×10^{-7} to 1×10^{-6} M and 1.5×10^{-6} to 4.5×10^{-6} M with a detection limit equal to 2.7×10^{-8} M and limit of quantification equal to 9.2×10^{-8} M. The simultaneous determination of curcumin and vitamin B_2 included a well resolved peaks, that provides rapid and selective analysis in the presence of vitamin B_2. Moreover, the practical application of the developed electrode was performed for the analysis of a natural food supplement for curcumin.

KEYWORDS

Carbon nanotubes; curcumin; sodium dodecyl sulfate; vitamin B_2; voltammetric sensor

Introduction

Curcumin is a yellow substance obtained from the rhizome of *Curcuma longa L*[1] that is widely used as a food additive, largely in canned foods, cakes, beverages and other dyeing applications.[2] This compound is well known for its biological and pharmaceutical properties such as antioxidant[3–4] anti-inflammatory[5] anticarcinogenic[6–7] and anti-human immunodeficiency viruses properties.[8] Curcumin also occupies a high place in ayurvedic medicine as a cleanser of the body.

Furthermore, this substance does not have toxic, genotoxic or teratogenic properties.[9] It is extensively used in the treatment of Alzheimer, multiple

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Analytical Chemistry

Sensitive and Selective Electrochemical Resolution of Tyrosine with Ascorbic Acid through the Development of Electropolymerized Alizarin Sodium Sulfonate Modified Carbon Nanotube Paste Electrodes

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An approachable and a selective electrocatalytic investigation of tyrosine (TR) with ascorbic acid (AA) in phosphate buffer solution (PBS) was done using a sensitive Poly Alizarin sodium sulfonate modified Carbon nanotube paste electrode (PASSMCNTPE). The morphological and elemental studies on PASSMCNTPE and bare carbon nanotube paste electrode (BCNTPE) were resolute through field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDX). The PASSMCNTPE shows excellent sensitivity, selectivity, stability, repeatability, and reproducibility for the electrochemical characterization of TR through cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The prepared sensor provides an elevated current response towards TR as compared to the BCNTPE. A plot of the anodic peak current of TR and the concentration of TR was obtained linearly in the range 1.4×10^{-4} M to 2×10^{-4} M with the limit of detection (LOD) 7.8×10^{-7} M and the limit of quantification (LOQ) 26×10^{-7} M respectively. The equipped sensor was also helpful for the quantitative and qualitative analysis of TR moiety in a pharmaceutical drug as a real sample.

Introduction

TR and AA are the most imperative fundamental moieties for the living organisms. TR is one of the conditional aromatic amino acid, which is found in numerous foodstuffs; also it is a precursor for the hormones, neurotransmitters, pigments and some needful proteins.[1–3] TR reveals many applications in the human body such as improvement of mental efficiency, maintenance of positive nitrogen balance,[4] photosynthesis, normalization of high blood pressure, curing of Parkinson's disease and Alzheimer's disease.[5,6] But an abnormality of TR in the living organisms causes high blood pressure, albinism, stress, lowering of body temperature, and some thyroid problems.[7,8] AA is also named as Vitamin C, is found in many food resources and utilized for some dietary supplements. AA has numerous utilities in the living bodies such as antioxidant properties, prevention of wounds, fabrication of some neurotransmitters, and curing of bone disorder (osteogenesis).[9–11] AA exposes some effects in the body such as gastric problems, scurvy, cardiovascular disease and Alzheimer's disease.[12,13] The structure of AA is shown in Scheme 1A.

Various techniques were reported for the examination of TR such as fluorimetry,[14] gas chromatography-mass spectrometry,[15] liquid chromatography-tandem mass spectrometry,[16] chemiluminescence,[17] spectrometric analysis,[18] and capillary electrophoresis,[19] but these methods were time consuming, tedious and costly as compare to electrochemical methods.[20–23] The electrochemical methods mainly depends on modified sensors, recent works presented many modified sensors likely Europium hexacyanoferrate film,[5] Boron-doped diamond electrode,[24] Nanostructures on gold electrodes,[25] Carbon electrode modified with a Nafion/TiO2-graphene composite film,[26] Poly (thionine) glassy carbon electrode,[27] Boron-doped diamond and diamond nanowire electrode.[28] They shows comparable detection limit with lesser activity. Hence our work is mainly focused towards the development of high sensing sensor for the electrochemical analysis of TR.

Electrochemical methods have been broadly used as approachable and selective analytical techniques for the analysis of the trace quantity of biologically significant samples, pharmaceutical moieties, and food samples based on chemically modified carbon based electrochemical sensors (CMCBES). The best properties of CMCBES are catalytic activity, determination of target moieties in presence of any other active species and they are very needful in the field of medicine.[29–41]

Now a day's Carbon nanotube (CNT) paste electrodes has a wide range of applications in the electrochemical investigation of electroactive species due to its prominent mechanical strength, high electrical conductivity, larger surface area, first-class chemical stability and distinctive electronic properties,[3,42,43] hence CNT was used as a main precursor for this work.

The Alizarin sodium sulfonate (ASS) or alizarin red-S is a water soluble aromatic quinine derivative with two OH groups, which acts as a coloring agent, pH indicator, surface modifier and artificial electron donor due to these characters electro-

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Research Article

Design of novel Surfactant Modified Carbon Nanotube Paste Electrochemical Sensor for the Sensitive Investigation of Tyrosine as a Pharmaceutical Drug

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Abstract

Purpose: The novel sodium dodecyl sulfate modified carbon nanotube paste electrode (SDS/CNTPE) was used as a sensitive sensor for the electrochemical investigation of L-tyrosine (TY).
Methods: The electrochemical analysis of TY was displayed through cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The surface morphology of SDS/CNTPE and bare carbon nanotube past electrode (BCNTPE) was reviewed trough field emission scanning electron microscopy (FESEM).
Results: The functioning SDS/CNTPE shows a voltammetric response with superior sensitivity towards TY. This study was conducted using a phosphate buffer solution having neutral pH (pH=7.0). The correlation between the oxidation peak current of TY and concentration of TY was achieved linearly in CV method, in the range 2.0×10^{-6} to 5×10^{-5} M with the detection limit 729 nM and limit of quantification 2.43 µM. The investigated voltammetric study at SDS/CNTPE was also adopted in the examination of TY concentration in a pharmaceutical medicine as a real sample with the recovery of 97% to 98%.
Conclusion: The modified electrode demonstrates optimum sensitivity, constancy, reproducibility, and repeatability during the electrocatalytic activity of TY.

Introduction

L-tyrosine (TY) is one of the standard aromatic amino acid found in some foodstuffs and living organisms; it performs as a building block of the proteins.[1-3] TY is acting as an originator of neurotransmitters, pigments, and hormones such as dopamine, thyroid and melanin.[4-7] TY facilitates to improve mental performances and attentiveness or remembrance; also TY is use to avoid depression or attention deficit disorder, high blood pressure, Parkinson's disease, alcoholism, and cocaine addiction and too helpful for photosynthesis. The abnormality of TY could cause albinism, alkaptonuria, low blood pressure, low body temperature and an underactive thyroid.[8] Some people have the low intensity of TY in their bodies because of the hereditary condition called phenylketonuria due to this body do not develops amino acid called phenylalanine.[9,10]

In the previous works numerous methods were evidenced, such as chromatographic studies, mass spectroscopic studies,[11-14] spectrophotometric studies[15,16] and electrochemical studies for the determination of biologically active scaffolds, in these studies, electrochemical studies[17-22] such as cyclic voltammetry (CV) and differential pulse voltammetry (DPV) shows excellent sensitivity, and they are trouble-free to handle in the laboratory circumstances, these are used to study the kinetics of a reaction, electron and ion transfer reactions.[23] Also, these techniques mainly depends on chemically modified electrodes that are working electrodes. Here we use multi-walled carbon nanotube (MWCNT) for the preparation of the working electrode because it shows excellent sensitivity, steadiness, high electrical conductivity and high surface area towards biologically active moieties.[24] The modification of bare carbon nanotube past electrode (BCNTPE) was done using SDS as an anionic surfactant material; it gives more excellent sensitivity and stability during the adsorption of the analyte[25] due to the hydrophobic and hydrophilic behavior. Hence the analysis of TY was carried out at sodium dodecyl sulfate modified carbon nanotube paste electrode (SDS/CNTPE). CV and DPV were also used to investigate the reaction mechanism of TY in the pharmaceutical drug as a real sample. The structure and oxidative reaction mechanism of TY at the SDS/CNTPE is shown in Scheme 1.

Materials and Methods

Materials

Silicone oil, Sodium hydroxide and SDS were purchased from Nice Chemicals, India. Disodium hydrogen

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Full Paper

Poly(Niacin) Based Carbon Nanotube Sensor for the Sensitive and Selective Voltammetric Detection of Vanillin with Caffeine

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Abstract-In the current work, a novel sensor was developed for the analysis of Vanillin (VN) by electrochemical polymerization of Niacin over the surface of carbon nanotube paste electrode. The features of electrode surface was studied using Field Emission Scanning Electron Microscopy (FE–SEM) images. Sweep rate variation study was conducted in the optimum pH (pH 7.0) for the evaluation of number of electrons involved in the electrochemical reaction and to investigate the mode of mass transfer phenomena. This investigation reveals that the electrode undergoes adsorption controlled mass transfer process. Based on the data obtained from the measurements the oxidation mechanism of VN was proposed. The prepared sensor was also applied for the simultaneous detection of VN and Caffeine (CF). Quantitative determination of VN was accomplished by cyclic voltammetric (CV) method. The corresponding value of limit of detection (LOD) and limit of quantification (LOQ) of VN was found to be 10.1×10^{-7} M and 3.3×10^{-6} M, respectively. In addition, the applicability of the proposed method was checked with the detection of VN in real sample with good recovery data.

Keywords- Cyclic voltammetry; Vanillin; Poly(Niacin); Real sample analysis

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RESEARCH ARTICLE

Electrochemical Fabrication of Poly (niacin) Modified Graphite Paste Electrode and its Application for the Detection of Riboflavin

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Abstract:

Objective:

A poly niacin (NN) modified graphite paste electrode was prepared through a simple electrochemical polymerization route for the determination of Riboflavin (RF)

Methods:

Electropolymerization technique was used for the preparation of a modified electrode. The electrochemical impedance spectroscopy (EIS) method was used to study the surface behaviors and conductivity of the bare and modified electrodes. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were used to study the electrochemical behavior of RF using 0.2 M PBS of 7.5 pH.

Results:

Poly niacin modified graphite paste electrode (PNNMGPE) provides more affinity towards RF detection with high sensitivity and selectivity over bare graphite paste electrode. RF calibration curve was obtained by LSV between 5.0 µM to 65.0 µM with 0.782 µM limit of detection (LOD) and 2.7608 µM limit of quantification (LOQ), respectively. Selective analysis of RF in the presence of ascorbic acid (AA) and dopamine (DA) was performed at PNNMGPE by the LSV method.

Conclusion:

The developed PNNMGPE was tested for RF analysis in a multivitamin tablet with good results. Furthermore, the developed electrode shows good stability and reproducibility.

Keywords: Poly niacin, Graphite paste electrode, Riboflavin, Voltammetry, Electropolymerization technique, Electrochemical impedance spectroscopy (EIS).

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1. INTRODUCTION

Riboflavin (RF) or vitamin B_2 is used as a dietary supplement and it is a water-soluble B group vitamin, and a a constituent of flavoenzymes [1, 2]. It plays an important role in human biochemistry and metabolism. It is not produced in the human body. It is obtained naturally through a food diet. RF is naturally found in nuts, milk, vegetables and fruits, meat, and eggs. Deficiency of RF in the human body can lead to eye and skin disorders, microcytic hypo-chronic anemia, night blindness (beriberi), pellagra or sometimes even death [3 - 7]. Also, RF overdose can cause oxidative damage to DNA and tissue by UV radiation exposure [7 - 11]. So it is important to develop a simple and sensitive analytical method to determine RF.

Existing methods in analyzing RF include chromatography, UV-spectrophotometry, chemiluminescence, Reversed-Phase-High-performance liquid chromatography,

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Regular Article

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Polymer Modified Carbon Paste Electrode as a Sensitive Sensor for the Electrochemical Determination of Riboflavin and Its Application in Pharmaceutical and Biological Samples

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Poly (threonine) modified carbon paste electrode (PTMCPE) can be used as a responsive and selective electrocatalytic sensor for the estimation of riboflavin (RF) by means of cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The proposed electrode creates a catalytic enhancement in redox behavior of RF when equated with bare carbon paste electrode (BCPE). Under optimized conditions, RF quantification at modified electrode has shown a detection limit of 1.78×10^{-7} M in the linear range of 0.2-1 µM and 1-5 µM. Simultaneous analysis of RF with folic acid (FA) and ascorbic acid (AA) shows well-separated peaks leading to a quick and selective analysis of RF. The fabricated sensor can be successfully applied to RF analysis in human blood serum and B- complex tablet with acceptable results.

Keywords: Riboflavin, Electrochemical sensor, Carbon paste electrode, Poly (threonine), Ascorbic acid, Folic acid

INTRODUCTION

Organic compound Riboflavin (RF, vitamin B_2) is essential for the natural metabolism in the human body [1]. The water-soluble RF, a component of flavoenzymes, plays a major role in biochemical reactions [2]. It has some pharmaceutical values and functions as an antioxidant [3], anti-inflammatory [4], and analgesic [5] compound. It is not produced in the body and hence it has to be supplemented through diet. The two components present in RF are flavin adenine dinucleotide and flavin mononucleotide. These components are essential for a number of flavoprotein enzyme reactions including the activation of other vitamins. RF is found in green vegetables, enriched flour, meat, nuts and eggs [6]. Insufficient ingestion of RF can have an adverse effect on health, resulting in numerous grave diseases such as microcytic hypo-chronic anaemia, night blindness (beriberi), pellagra or sometimes even death [7]. Obviously, it is of much significance to initiate a straightforward, simple, consistent and successful process for RF determination.

Several procedures have been applied for the estimation of RF, including fluorescence [8-11], chemiluminescence [12,13] and capillary electrophoresis [14]. These approaches can be utilized for the quantification of RF, but they are tedious, expensive and time consuming [15]. Electrochemical processes have gained importance in the quantitative estimation of RF because of their simple, sensitive, cheap and quick response [16-18]. The chemically modified electrodes afford a device to advance the performance of electrodes and enormous functional materials as modifiers for vitamin sensors [19-20]. The nanoparticles of metallic or semiconducting materials with conducting polymer find massive applications in catalysis, electronics, and sensors [21-23]. Based on the constituent polymer and the metal introduced, physical and chemical properties of the electrode can be studied. Accordingly, setting a polymer with nanoscale material, nano-electronic

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Arginine Electropolymerized Carbon Nanotube Paste Electrode as Sensitive and Selective Sensor for Electrochemical Determination of Vanillin

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Abstract

Poly(Arginine) modified carbon nanotube paste electrode (PAMCNTPE) was prepared and it was approachable and discriminatory electrocatalytic sensor for Vanillin (VAN) determination using Linear Sweep Voltammetry (LSV), Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV). The surface morphology of the formulated sensor is investigated by Field Emission Scanning Electron Microscope (FESEM). The tailor made electrode has exposed an exceptional electrocatalytic effect to VAN detection when compared to bare carbon nanotube paste electrode (BCNTPE). Under the optimized circumstances, the quantification of VAN at the developed electrode has revealed the linear range 2 $\times 10^{-6}$ M to 1×10^{-5} M and 1.5×10^{-5} M to 4.5×10^{-5} M and a limit of detection 3.3×10^{-8} M. Instantaneous resolving of VAN and Caffeine (CAF) shows a well separated peaks at 0.508 V and 1.281 V. Applicability of the developed electrode is studied using food sample, shows the recovery in the range of 95.92%to 99.73%, this indicates that the modified electrode is having better analytical performance and can be used for the determination of VAN in commercial food samples.

1. Introduction

Vanilla, one of the world's best flavor extract obtained primarily from Vanillia Planifolia. Among 110 species hardly 3 species of Vanillin (VAN) finds commercial importance. Vanillia planifola, Vanilla tahitensis and Vanilla pompon [1]. The fragrance and essence of vanilla extract is mostly due to the occurrence of Vanillin, which is present in the concentration of 1.0 to 2.0% w/w in cured Vanilla pods [3]. VAN (4- hydroxy - 3- methoxybenzaldehyde) is one of the foremost components of natural Vanilla. Every year more than 12,000 tons of Vanillin produced, however lesser than 1% of it is from natural Vanilla. The remaining is synthesized from either chemical or biochemical processes [1-2]. VAN is used extensively in beverages, foods, perfumery, and confectionary and even in pharmaceutical drugs like aldomet, L-dopa etc. [3-4]. It also finds applications in soft drinks as a preservative, in corrosion reactions as an inhibitor and in methacrylate polymerization reaction as a catalyst [5]. However, extreme intake of VAN can result in vomiting, headache, nausea, and also potential damage to liver and kidney [6].

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Fabrication of the Tartrazine Voltammetric Sensor based on Surfactant Modified Carbon Paste Electrode

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ABSTRACT

In this paper, TX-100 modified carbon paste electrode (TX-100MCPE) was fabricated for the resolution of tartrazine (TZ). The modified electrode showed magnificent electrocatalytic activity towards TZ. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) was used to characterize the electrochemical properties of modified electrodes. CV studies point out that the oxidation of TZ at the modified electrode surface was irreversible, adsorption controlled, and reaction which involves one electron transfer. The effects of different experimental parameters like pH, Scan rate, Concentration on the voltammetric response of TZ were investigated. After optimizing the experimental parameter, the oxidation peak current of TZ was linear to its concentration in the range of 6×10^{-6} to 1×10^{-4} M, and the detection limit was 11.14×10^{-7} M. The modified electrode was found to be, inexpensive, provide good stability and reproducibility.

Keywords: *Tartrazine, Carbon paste electrode, TX-100, cyclic voltammetry, Differential pulse voltammetry*

INTRODUCTION

Color is a major assign when it comes to food choices. Food colorants are added to food to enhance its appealing, and its applicability. TZ is an orange-colored, water soluble, Synthetic azodye widely used in food products, drugs, and pharmaceuticals. Synthetic azodyes with aromatic structures were harmful to human health [1]. TZ can cause diarrhea, anxiety, allergies and even cancer if they overly ingest [2-3]. It became an analytical challenge because of increasing the legal restriction.

There are many methods have been used for the resolution of TZ such as spectrophotometry [4] high-performance liquid chromatography [5] and capillary electrophoresis [6] and electrochemical techniques [6-9].

The Electrochemical methods traditionally have found broad applications in sample analysis due to the short analysis time, low power consumption and inexpensive equipment. CV is the most widely used electroanalytical technique for the qualitative information about electrochemical reactions.

Carbon electrodes are widely used in electroanalysis due to their wide potential window, chemical inertness, low cost and suitability for various sensing detection applications [10-20]. Among these carbon electrodes, carbon paste electrode (CPE) was widely used because due to the low cost, obtaining a new reproducible surface, etc. There for over the past decades, CPEs containing various modifiers was widely used and applied in the resolution of different analytes [21-23]. CPEs can provide a suitable electrode substrate for preparation of modified electrode.

There are a number methods reported for the resolution of TZ using various modified electrodes includes poly (p-amino benzene sulfonic acid)/Zinc oxide nanoparticle [24] Multiwalled carbon nanotube modified pyrolytic graphite electrode [25], nanogold modified carbon paste electrode [26], etc.

The surfactant has been widely used in chemistry. Due to its distinct structure and being surface active, surfactants are used in the electrochemical investigation. The modification of electrode by surfactant increases the electron transfer rate and also improves the detection limit. In this study, an electrochemical sensor was developed based on TX-100 surfactant modified with carbon paste electrode for the resolution of TZ.

The electrochemical behavior of TZ was studied by using CV and DPV. The oxidation mechanism

CHAPTER 6

Fabrication, characterization and application of poly(acriflavine) modified carbon nanotube paste electrode for the electrochemical determination of catechol

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1. Introduction

Catechol (CA), generally known as pyrocatechol or benzene-1,2-diol and belonging to the simple phenolic compounds, has a predominant significance in biological and ecological systems like bearing antiviral and antifungal properties, which affects some of the enzyme activities and root growth of the plant [1]. The main source of CA is basically from nature via plants like tobacco, tea, coffee, and the tannin layer of mycorrhiza of the douglas fir, and a small quantity of CA is present in some fruits and vegetables like apples and potatoes [2–4]. CA has a major role in various industries such as pharmacy; in the photography industry as a developing agent in photographic negative film; in rubber and oil industries as an intermediate for the antioxidants of rubber, olefins, and polyolefins, and in the industries of dyes, perfumes, detergents, and pesticides [5, 6]. Even with all these benefits, it is a hazardous compound and toxic to human beings, flora, fauna, and aquatic species at low concentrations [7]. Moreover, it cannot be degraded easily and hence it is considered as pollutants according to the European Union and US Environmental Protection Agency [8]. CA in contact with skin brings about eczematous dermatitis [9]. Exposure to CA also affects the central nervous system causing depression, hampering DNA replication, and causing chromosomal abnormalities [10, 11]. Therefore, it's essential to determine CA by establishing sensitive and consistent techniques.

Recently, numerous techniques have been applied for the determination of CA involving spectrophotometry [12], fluorimetry [13], gas chromatography [14], high-performance liquid chromatography [15], flow-injection chemiluminescence [16], and electroanalytical techniques [17, 18]. Contrary to the electroanalytical techniques, all

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Original scientific paper

Electrochemical analysis of indigo carmine using polyarginine modified carbon paste electrode

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Abstract

Suitable electrocatalytic method is established for the selective determination of indigo carmine (IC) at polyarginine modified carbon paste electrode (PAMCPE). Surface morphological study of bare carbon paste electrode (CPE) and PAMPCE is done by field emission scanning electron microscopy (FESEM). The influence of different parameters such as IC concentration, solution pH and potential scan rate on the electrode responses is studied using cyclic and differential pulse voltammetry techniques. The prepared PAMCPE shows better electrochemical response towards IC than CPE. No interference is noticed at simultaneous presence of IC and riboflavin (RF) in the solution. The electrocatalytic current of IC at PAMPCE is varied linearly with its concentration in two separate ranges, from 2×10^{-7} to 10^{-6} M, and 1.5×10^{-6} to 3.5×10^{-6} M. Limits of detection (LOD) and quantification (LOQ) are determined as 2.53×10^{-8} and 8.43×10^{-8} M, respectively. The developed PAMCPE is showing successful reproducibility and stability. It is also found sensitive and reliable for trace amounts of IC in some real water and food samples. Since preparation of PAMCPE sensor is simple and easy, it could become a part of the standard method for determination of IC in real samples.

Keywords

Carbon paste; electropolymerization; food dye; real samples; cyclic voltammetry; differential pulse voltammetry

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Electroanalytical Determination of Tinidazole by using Surface Modified Carbon Nano Composite based Sensor

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ABSTRACT

As an antibiotic, tinidazole (TNZ) is usually consumed to reduce the bacterial infection; thus, qualitative determination of the TNZ is very significant. Thus, in this article, the development of voltammetric sensor based on poly-threonine-modified carbon nanotube-mixed graphene paste electrode (PTRMCNTMGPE) for the detection of TNZ was reported. The PTRMCNTMGPE displayed a boosted electrocatalytic effect regarding the voltammetric signal of the TNZ (pH 7.0) compared to the bare electrode. The morphology of the proposed electrodes was characterised by field emission scanning electron microscopy. The charge transfer resistance of the designed electrode was studied through electrochemical
impedance spectroscopy. The impact of pH and effect of scan rate was studied. The scan rate study reveals the reduction process of the TNZ was controlled by diffusion. The designed electrode yielded low detection limit (0.2 μM) for TNZ. The proposed electrode exhibited a good reproducibility, repeatability, selectivity and an antifouling feature. The practicability of the developed sensor was explored by detecting the TNZ in tablet and blood serum samples.

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KEYWORDS
Carbon nanocomposite; voltammetric study; tinidazole; poly-threonine-modified electrode; electropolymerisation

1. Introduction

Antibiotics have gained a major place among medicine due to their activity of curing diseases related to microorganisms and have ubiquitous usage all over the world. Tinidazole (TNZ) is an anti-parasitic drug and nitroimidazole derivative used against protozoa and bacterial infection. It is utilised to treat giardiasis, amoebiasis, and bacterial vaginosis [1,2]. It is most commonly consumed to reduce trichomoniasis, and against metronidazole-resistant trichomoniasis [3,4]. It is prescribed in the adult's periodontitis and is effective rather than metronidazole against periodontal infection [5]. The adverse effects associated with TNZ are headache, giddiness, anorexia, diarrhoea, bitter taste, and physical impotence [6]. Therefore, to analyse the concentration of the TNZ, an inexpensive, quick response, and a simple electrochemical approach is needed.

The pharmaceutical analysis has received an enormous interest due to their importance in quality control of the pharmaceutical products. Thus, previously, several analytical methods were published for the determination of TNZ such as chromatography technique [7–9], spectrophotometry [10–13], and capillary electrophoresis [14,15]. The aforementioned methods are sensitive but have some limitations such as requirements of high priced instruments, large amount of chemicals, time utilising procedures, and expert technicians essential to handle instruments. Hence, to defeat the above limitations, electrochemical methods are the best alternative for the detection of the targeted molecules. Electrochemical methods are the most significant technique in the field of analytical chemistry [16–22]. The electroanalytical techniques are found to be significant compared to the optical methods [23–28]. Voltammetric techniques are one of the simplest and sensitive techniques among the electrochemical methods. Cyclic voltammetry (CV) is one of the main classes of the voltammetric technique [29–33]. Therefore, the development of a voltammetric method for the detection of the TNZ is crucial.

The field of nanotechnology has become progressively one of the most favourable tools in analytical chemistry and nanomaterial gained lots of attention from the modern electrochemists. Carbon nanotubes (CNTs) and graphene are the carbonaceous nanomaterial that possesses enormous physicochemical, electrical, and mechanical properties due to this it is usually utilised in the field of electrochemistry as a sensing material [34,35]. The synergetic combination between the CNTs and graphene with the modifier provides a large surface area, antifouling property, signal enrichment, and rapid electron transferability [36–41]. Electropolymerisation and immobilisation are simple modification methods. Electropolymerisation is an easy method that involves the thin conducting film deposition on the electrode surface by the controlled scanning [42,43]. Hence, by utilising the simple electropolymerisation technique, it is essential to construct the modified electrode for the detection of the analyte.

In this current research article, a facile electrocatalyst based on poly-threonine-modified carbon nanotube-mixed graphene paste electrode (PTRMCNTMGPE) was constructed to enhance the electrochemical response of the TNZ. The PTRMCNTMGPE exposed the enriched electrocatalytic activity towards the detection of the TNZ than the bare CNTMGPE (BCNTMGPE). The field emission scanning electron microscopy (FE-SEM) image proves the electrodeposition of the PTR on the BCNTMGPE and electrochemical impedancde spectroscopy (EIS) provides the resistance of the electrode. The modified electrode yielded a low detection limit (DL) for TNZ via differential pulse voltammetry (DPV) method.

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Rapid Electrochemical Monitoring of Tyrosine by Poly (Riboflavin) Modified Carbon Nanotube Paste Electrode as a Sensitive Sensor and its Applications in Pharmaceutical Samples

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Abstract: A poly(riboflavin) modified carbon nanotube paste electrode (PRFMCNTPE) is employed as a compatible and electrocatalytic sensor for the determination of Tyrosine (TYR). The analysis and assessment are carried out through differential pulse voltammetry (DPV) and Cyclic Voltammetry (CV). The surface of the intended sensor is examined through Field Emission Scanning Electron Microscopy (FE-SEM). The modified electrode shows the outstanding electrocatalytic effect for TYR with high selectivity and sensitivity as compared to carbon nanotube paste electrode (CNTPE). The electro-oxidation peak current of TYR and its concentration is found linear from 2 µM to 10 µM with a detection limit (LOD) of 0.45 µM. The developed sensor is productively applied for the determination of TYR in pharmaceutical samples like Tyrosine capsules. The adapted electrode shows good stability, excellent reproducibility, and remarkable sensitivity.

Keywords: Poly(riboflavin); tyrosine; electrochemical sensor; carbon nanotube paste electrode; voltammetry.

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1. Introduction

Amino acids are the building blocks of proteins that make up most parts of our body. They are highly essential for developing human organs such as muscles, hormones, and the nervous system [1]. Among the amino acids, Tyrosine (TYR) (4- hydroxyphenylalanine) is a well-known essential aromatic amino acid for nutritional balance in herbivore's bodies. A human being's healthy state is correlated with the amount of TYR present in the body [2-3]. TYR is determined as a precursor for thyroxine, dopamine, adrenaline, and non-adrenaline hormones or neurotransmitters [4-5]. It is a vital constituent of proteins, which is indispensable in humans nutrition for maintaining and establishing a supportive balance of nitrogen in the human body [6-7], and its deficiency may produce hypochondria, depression [8-9]. A high TYR concentration in the culture medium can cause increased sister chromatid exchange, and a high level of TYR may also lead to Parkinson's disease [10-11]. The low intensity of TYR

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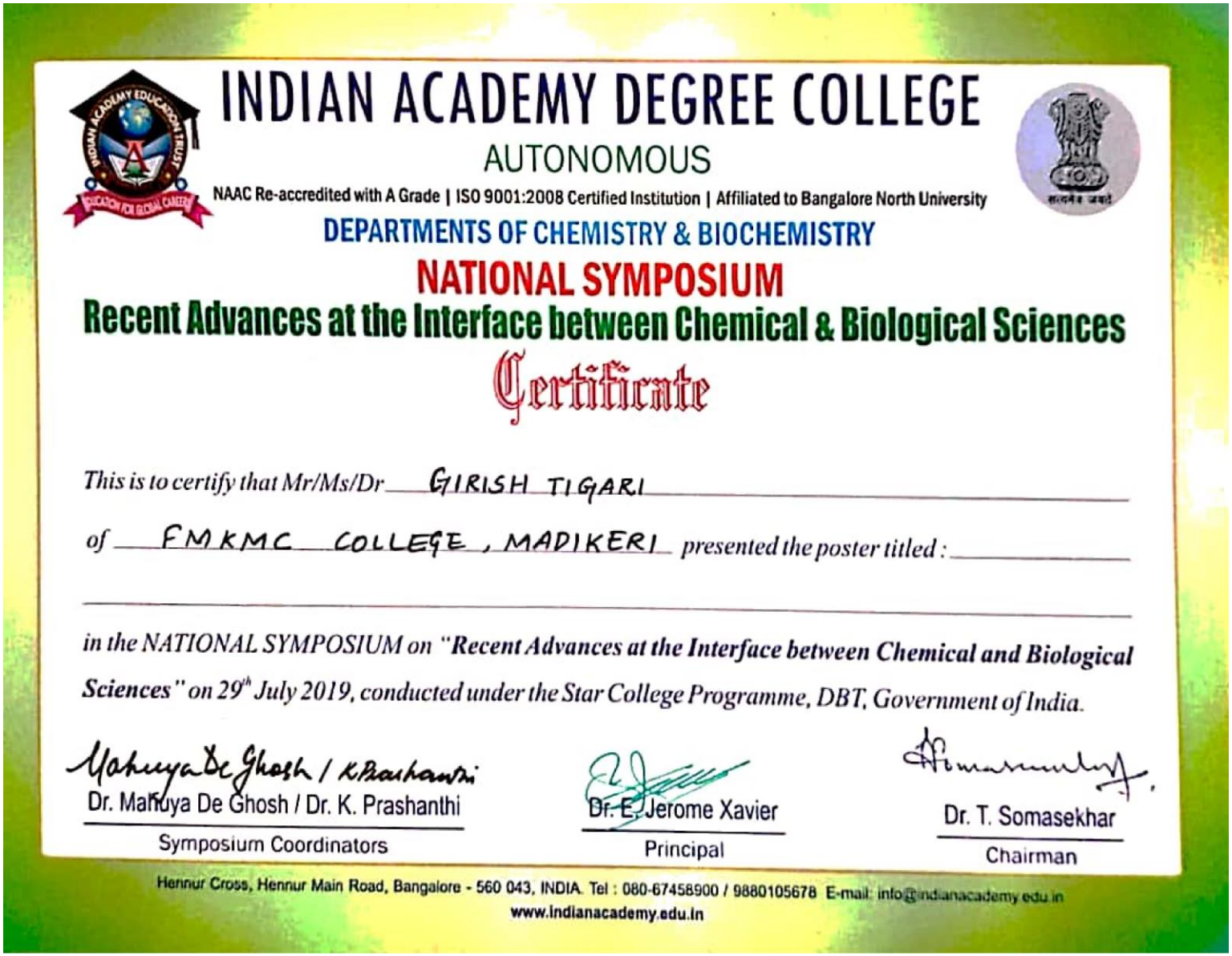

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